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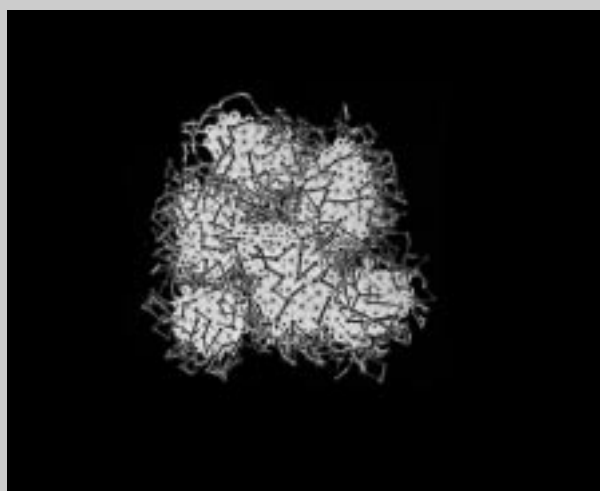
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Full Paper: Computer simulation modelling of a flexible comb copolymer with attractive interactions between the monomer units of the side chains is performed. The conditions for the coil-globule transition, induced by the increase of attractive interaction, ε , between side chain monomer units, are analysed for different values of the number of monomer units in the backbone, N , in the side chains, n , and between successive grafting points, m . It is shown that the coil-globule transition of such a copolymer corresponds to a first-order phase transition. The energy of attraction (ε) required for the realisation of the coil-globule transition decreases with increasing n and decreasing m . The coil-globule transition is accompanied by significant aggregation of side chain units. The resulting globule has a complex structure. In the case of a relatively short backbone (small value of N), the globule consists of a spherical core formed by side chains and an enveloping shell formed by the monomer units of the backbone. In the case of long copolymers (large value of N), the side chains form several spherical micelles while the backbone is wrapped on the surfaces of these micelles and between them.



Snapshots of globules formed by comb copolymers with $n = 4$, $m = 4$, $\varepsilon_{SS} = 0.6$ and different values of N : $N = 2048$.

Microphase Separation within a Comb Copolymer with Attractive Side Chains: A Computer Simulation Study

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1 Introduction

The comb copolymers considered here are molecules consisting of a flexible backbone chain densely grafted with flexible side chains. The parameters characterising its structure are the number of monomer units in the backbone, N , in the side-chains, n , and between successive grafting points, m .

As a result of the excluded volume interactions, the conformation of a comb copolymer differs from the conformation of a linear macromolecule.^[1] Theoretically^[2–5] and by means of computer simulations^[6–9] it was shown that as a result of the excluded volume interaction between monomer units of side chains, the molecule is swollen with a strongly increased stiffness of the backbone. In the case of semiflexible side chains, computer

simulations show that the excluded volume interactions give rise to a cylindrical brush-like structure,^[9] in agreement with experimental observations.^[10] In the case of comb copolymers absorbed on a flat surface, the excluded volume interaction may lead to an even stiffer structure.^[7] But not only that, in some cases it may also lead to bending and twisting resulting in spiral-like conformations. Such structures were observed experimentally and by computer simulations^[11,12] and are described theoretically in ref.^[13]

Comb copolymers with attractive interaction between the side chains (e.g., molecules consisting of hydrophobic side chains and a hydrophilic backbone in water) are currently a subject of much interest.^[14–19] It is clear that an attractive interaction between side chains can induce a

contraction of the macromolecule and its collapse to the globular state. By means of computer simulations it was shown in ref.^[20] that the collapse transition of such a molecule proceeds with a sharp reduction in macromolecular size over a narrow energy interval.

In the present paper we analyse the coil-globule transition of comb copolymers with attractive interaction between side chains employing the bond-fluctuation model.^[21,22] We will supplement the analysis of ref.^[20] by a thorough analysis of the properties of the coil-globule transition as a function of the length of the side chains and the grafting density, i.e., parameters n and m . We will investigate in detail the structure of the emerging globule varying the length of the backbone (N) as well.

The next section contains the description of the model used for the computer simulations. The results and discussion are given in section 3.

2 Model

For the simulation of flexible polymer chains we employ the so-called bond-fluctuation model (BFM).^[21,22] In the BFM model the polymer chain is confined to a cubic lattice and has a variable bond length, b . Each effective monomeric unit occupies eight neighboring lattice sites of a simple cubic lattice and each lattice site can only be part of one monomeric unit. The polymer chain is represented by a sequence of effective bond vectors, b , belonging to the set $\{b\}_{d=3} = \{P(2,0,0); P(2,1,0); P(2,1,1); P(2,2,1); P(3,0,0); P(3,1,0)\}$, where $P(i_x, j_y, k_z)$ represents the set of all permutations and sign combinations of $\pm i_x, \pm j_y, \pm k_z$. In this case, the set of bond vectors $\{b\}$ connecting two successive monomers, contains 108 allowed vectors b with five different bond lengths:

$$b = 2, \sqrt{5}, \sqrt{6}, 3, \sqrt{10}$$

Thus, the length of the bond between two neighboring monomeric units can fluctuate between a lattice spacing of $b = 2$ and $b = 10^{1/2}$.

In correspondence with the main objective of this paper, the polymer consists of a backbone with N monomeric units and side chains of n monomeric units, equidistantly grafted on the backbone with the distance between grafting points equal to m .

The interaction between monomer units belonging to side chains (S) or backbone (B) is modeled by the following stepwise potential:

$$u_{ij}(r) = \begin{cases} \infty & r < 2 \\ -\varepsilon_{ij} & 2 \leq r \leq \sqrt{10} \\ 0 & r > \sqrt{10} \end{cases} \quad (i, j = B, S)$$

in which r is the distance between monomer units in a lattice spacing.

We assume that the monomer units of the backbone interact with the side chain units and with each other only via excluded volume interaction, i.e., $\varepsilon_{SB} = \varepsilon_{BB} = 0$, whereas the monomer units of the side chains attract each other. By increasing this attractive energy, ε_{SS} , we induce the transition from an expanded coil to a compact globular state.

As usual, the Monte-Carlo procedure consists of choosing a monomeric unit at random; then the unit tries to jump randomly, covering the distance of one lattice spacing, into one of the neighboring lattice sites. This move is only acceptable if both the bond length restrictions and the self-avoidance conditions are obeyed. The transition to a new configuration is accepted according to the standard Metropolis criterion with the transition probability $P = \min\{1, \exp(-\Delta E)\}$, where ΔE is the energy difference between two consecutive configurations.^[23]

The calculations were carried out using a three-dimensional cubic cell with usual periodic boundary conditions. The length of the backbone was varied from $N = 64$ to $N = 2048$. The degree of polymerization of the side chains and the distance between their grafting points were varied within the ranges: $n = 4-12$ and $m = 4-8$, respectively. To characterise the conformational state of the macromolecule at different values of ε_{SS} , we calculated the mean-square radius of gyration of the macromolecule, $\langle R^2 \rangle$, and the mean-square radius of gyration of its backbone, $\langle R_b^2 \rangle$. Simultaneously, to analyse the side chain aggregation process accompanying the coil-globule transition, we calculated the average aggregation number $\langle M \rangle$ defined as the number of monomer units of side chains belonging to the same cluster. We consider that the i^{th} and j^{th} side-chain monomer units are part of the same cluster if the distance between them is not longer than $10^{1/2}$, i.e., the cut-off distance of potential u_{ij} .

The results of the calculations were averaged over a set of k independent configurations obtained after a long equilibration of system. The sample standard deviation over this set was calculated. The number k was taken so that the sample standard deviation was less than 5 percent.

3 Results and Discussion

First of all, we study the dependence of the properties of the coil-globule transition on the structural parameters of the comb copolymer, i.e., on the length of the side-chain (n) and on the grafting density σ (by definition, σ is inversely proportional to the number of monomer units between grafting points: $\sigma = 1/m$).

Figure 1a and 2a show the dependencies of the swelling ratio α^2 (determined as the ratio of the radius of gyration, $\langle R_b^2 \rangle$, of the backbone chain to the radius of gyration, $\langle R_0^2 \rangle$, of the corresponding linear macromolecule with excluded volume interaction), on the energy of attractive

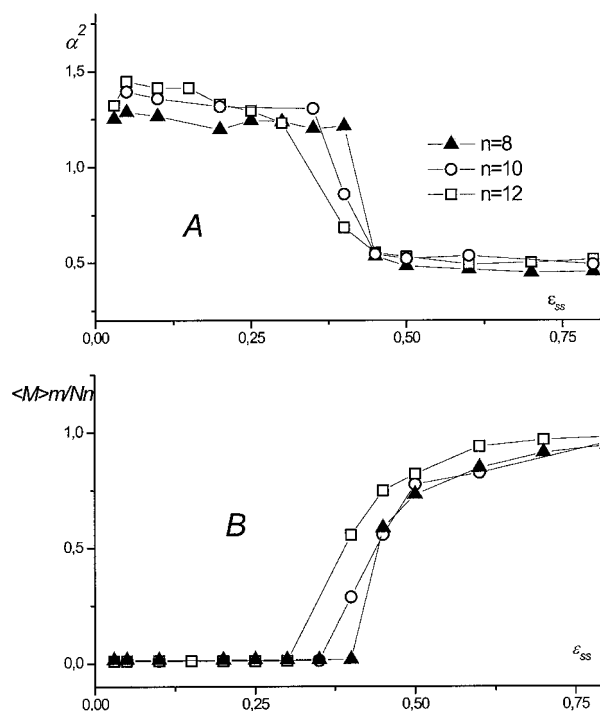


Figure 1. Behaviour of the radius of gyration of the backbone $\langle R_b^2 \rangle / \langle R_0^2 \rangle$ (a) and the fractional aggregation $\langle M \rangle m / Nn$ (b) as a function of the side chain interaction ϵ_{ss} for comb copolymers with $N = 64$, $m = 6$ and different values of n .

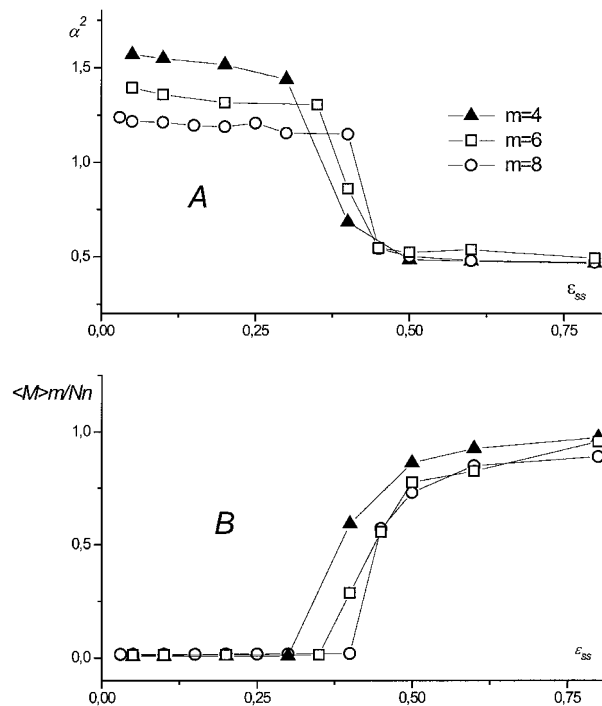


Figure 2. Behaviour of the radius of gyration of the backbone $\langle R_b^2 \rangle / \langle R_0^2 \rangle$ (a) and the fractional aggregation $\langle M \rangle m / Nn$ (b) as a function of the side chain interaction ϵ_{ss} for comb copolymers with $N = 64$, $n = 10$ and different values of m .

interaction (ϵ_{ss}) for different values of n (Figure 1) and m (Figure 2). Figure 1b and 2b present the corresponding dependencies of the average value of the maximum aggregation number, $\langle M \rangle$, divided by the total number, Nn/m , of side chain monomer units in the chain. The ratio $\langle M \rangle m / Nn$ characterises the fraction of side-chain monomer units entering into the cluster of average size. It is equal to zero if the side chain monomer units do not associate at all; and equal to unity if all these units are assembled into one cluster.

At small values of ϵ_{ss} , the comb copolymer stays in the swollen coil state. In correspondence with theory and computer experiments^[3,6,10] α^2 increases with an increasing number of monomer units in the side chain (n) and increasing grafting density, (σ). When the attractive interaction between the side chains (ϵ_{ss}) becomes strong enough, the macromolecule undergoes a collapse transition. This transition is rather sharp and proceeds in a narrow range of ϵ_{ss} values. The critical value, $(\epsilon_{ss})^{cr}$, of the coil-globule transition slightly decreases with increasing n and σ .

The coil-globule transition is accompanied by the aggregation of side chain monomer units into micelles with different aggregation number, M . In the region of the coil-globule transition the average aggregation number of such micelles grows sharply. Furthermore, at sufficiently high values of ϵ_{ss} (above the critical point $(\epsilon_{ss})^{cr}$) all monomer units of the side chains form a single micelle (see Figure 1b and 2b).

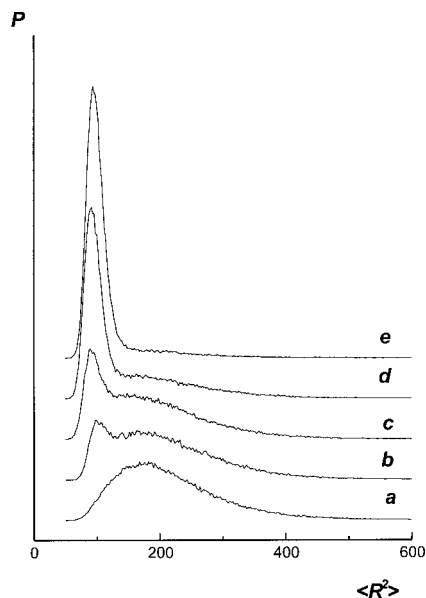


Figure 3. Probability distribution of the radius of gyration $\langle R^2 \rangle$ of the comb copolymer for molecules with $N = 64$, $n = 10$, $m = 6$ at different values of the side chain interaction energy ϵ_{ss} : 0.385 (a); 0.391 (b); 0.393 (c); 0.396 (d); 0.398 (e).

Figure 3 shows the probability distribution for the radius of gyration, $\langle R^2 \rangle$, at different energies, ϵ_{ss} . Each distribution was calculated over 10^6 independent configurations on the trajectory of consecutive states separated

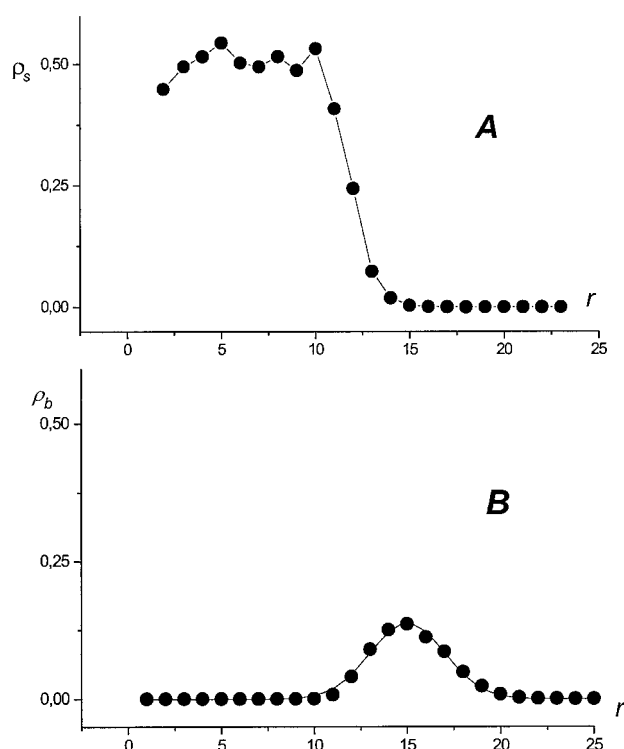


Figure 4. The local density ρ_i of side-chain (a) and backbone (b) monomer units as a function of distance r from center of gyration of the comb copolymer ($N = 512$, $n = 10$, $m = 6$, $\varepsilon = 0.6$).

by 10^3 Monte-Carlo steps. One can see that inside the region of the coil-globule transition (at intermediate values of ε_{SS} , see Figure 3b) the probability distribution has two maxima corresponding respectively to the coil and the globular state of the macromolecule. According to the general definition,^[24] the bimodality of the distribution in the transition region means that the coil-globule transition should be classified as a first order phase transition (see Figure 3). Generally speaking, the character of coil-globule transition in comb copolymer with attractive side chains depends on parameters n and m . The detailed analysis of dependence of sharpness of coil-globule transition on the length and density of grafting of side chains will be presented in forthcoming publications.

The globule of the comb copolymer chain with attractive side chains has a complex structure. To analyze this we calculated the local density, ρ_i , of monomer units of different types ($i = S, B$) as a function of distance, r , from the center of gyration of the globule. Typical results for a macromolecule with $N = 512$, $m = 10$, $n = 6$ and $\varepsilon_{SS} = 0.6$ are given in Figure 4. As can be seen, the ρ_S of side-chain monomer units is almost constant for $r < 10$ (r is always measured in lattice spacing). From $r = 10$, ρ_S drops gradually until $\rho_S = 0$ at a distance $r \approx 15$. On the other hand, the density of backbone monomer units (ρ_B) is equal to zero for the whole range of r values except for a rather narrow interval around $r \approx 15$. From these calcu-

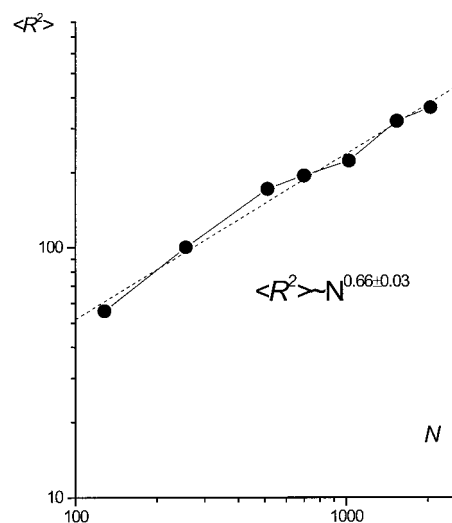


Figure 5. Radius of gyration $\langle R^2 \rangle$ of the comb copolymers as a function of the backbone chain length N for $n = 4$, $m = 6$ and $\varepsilon = 0.6$.

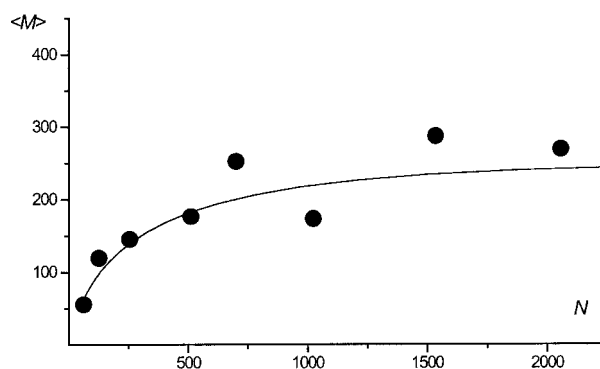


Figure 6. Average aggregation number $\langle M \rangle$ as a function of the backbone chain length N for comb copolymers with $n = 4$, $m = 6$ and $\varepsilon = 0.6$.

lations one can conclude that in the case under consideration the central part of the globule can be considered as an approximately spherical micelle formed by monomer units of the side chains. The monomer units of the backbone are situated in the enveloping shell of this micelle.

To analyse the dependence of the structure of the globule on the degree of polymerization, N , of the backbone, we performed a set of calculations whose results are presented in Figure 5 and Figure 6 for $n = 4$, $m = 4$ and $\varepsilon_{SS} = 0.6$. In Figure 5, the dependence of $\langle R^2 \rangle$ on N is given. The scaling exponent for the dependence of $\langle R^2 \rangle$ on N indicates that the comb copolymer molecule is in the compact globular state: $\langle R^2 \rangle \approx N^{0.66 \pm 0.03}$.

Figure 6 shows the dependence of the aggregation number $\langle M \rangle$, of side-chain monomer units within the globule, on N . As can be seen, the value of $\langle M \rangle$ first increases, and then, from $N \approx 200$, seems to saturate. This fact indicates that at large values of N several micelles are formed within the globule. The number of

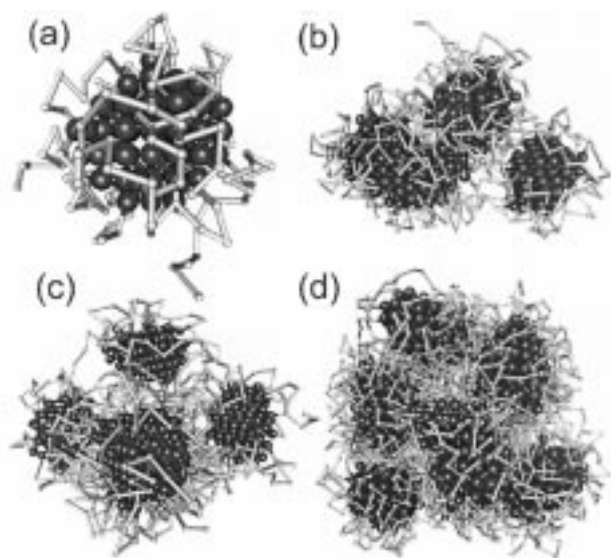


Figure 7. Snapshots of globules formed by comb copolymers with $n = 4$, $m = 4$, $\varepsilon_{ss} = 0.6$ and different values of N : $N = 128$ (a), 512 (b), 700 (c), 2048 (d).

such micelles increases with increasing number of monomer units in the backbone. Figure 7 shows typical snapshots of collapsed comb copolymer molecules with $m = 4$, $n = 4$ and different values of N . As can be seen, at low values of N the side chains form a single micelle, while at high values of N they are organized into a few dense micelles with the backbone chain wrapped on the surfaces of these micelles and between them.

It is easy to give an estimate for the maximum value of the monomer units in the backbone, N_{max} , for the macromolecule whose globular state contains a single spherical core. Indeed, the volume of a single spherical micelle of radius, R_m , formed by a comb copolymer should be equal, on the one hand to $\frac{4\pi}{3}R_m^3$, and on the other hand to the total volume of monomer units entering the globular core: $n \frac{N}{m} a^3$, where a is the size of a monomer unit. Therefore,

$$n \frac{N}{m} a^3 \sim \frac{4\pi}{3} R_m^3 \quad (1)$$

In general, within a dense cluster the chains can obey Gaussian statistics (strong segregation limit) or can be totally stretched (superstrong segregation limit).^[25] Therefore, the R_m of a spherical micelle will be in the range:

$$n^{2/3} a < R_m < na \quad (2)$$

Combining Equation (1) and (2) gives the following estimate for the maximum length, N_{max} , of the backbone above which the micelle should split into two or more different spherical micelles:

$$\frac{4\pi}{3} nm < N_{max} < \frac{4\pi}{3} n^2 m \quad (3)$$

Hence, the maximum value of the aggregation number, M_{max} , of the spherical micelle is:

$$\frac{4\pi}{3} n^2 < M_{max} < \frac{4\pi}{3} n^3 \quad (4)$$

For the system under consideration ($n = 4$, $m = 4$) Equation (3)–(4) imply that N_{max} and M_{max} for a stable single spherical micelle should be within the range 64–256. In our computer experiment the splitting of the micelle is observed already for macromolecules with $N = 256$ (Figure 7): the globule of such macromolecule contains two micelles. On the other hand, the aggregation number of the micelles in the case of long macromolecules with $N = 1536$ –2048 is rather close to the value of the maximum aggregation number, M_{max} , for the spherical micelle in the superstrong segregation limit. Thus, within the globule of a long comb copolymer, the side chains are segregated in micelles with the highest possible aggregation number. Within such micelles the side chains are almost fully stretched (see Equation (2)). The possibility of realizing such a regime was described in ref.^[25] for diblock copolymer micelles, where it was referred to as the superstrong segregation regime. It was shown^[26] that in the case of extremely strong attraction in the superstrong segregation regime, the fully stretched chains could form micelles of non-spherical shape with an aggregation number higher than that determined from the space-filling condition of Equation (1). In the case under consideration, with increasing degree of polymerization, N , the side chains prefer to split into different spherical micelles rather than form a non-spherical micelle. However, one could imagine that under some conditions (for example, at high attractive interaction between the side chains and a high degree of polymerization of the backbone) the shape of the cluster formed might change. A detailed analysis of the shape of the clusters as a function of the attractive interaction between the side chains and the structural parameters of the comb copolymer will be presented in a future publication.

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